EFFICACY OF THE FENTON REACTION FOR DEGRADING ALLURA RED AZO DYE: APPLICATIONS FOR USE IN HAIR SALON GREYWATER TREATMENT SYSTEMS

A Thesis
by
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Abstract

EFFICACY OF THE FENTON REACTION FOR DEGRADING ALLURA RED AZO DYE: APPLICATIONS FOR USE IN HAIR SALON GREYWATER TREATMENT SYSTEMS

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Azo dyes are one of the most common dyes used in the world. Traditional methods of removing azo dyes are ineffective, and some azo dyes have been found to be harmful to humans and the environment. This study looked at degrading the azo dye Allura red AC using the Fenton reaction. Of the conditions tested, the most effective for dye degradation involved ferrous sulfate in the range of 0.54 mM to 0.11 mM, and hydrogen peroxide in the 0.404 mM to 0.0404 mM range. The pH levels 2, 5, and 7 were analyzed with and without the buffers phosphate and citrate. For all cases, pH 2 was ineffective at degrading dye. The conditions where the solution was adjusted to pH 5 with and without phosphate degraded dye well, but pH 7 without buffers was the most effective. These findings are unexpected because the literature around the Fenton reaction states it is ineffective at pH levels near neutral.

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I would like to thank my committee chairperson, Dr. James Houser, for setting aside a time every week to discuss this thesis and for providing guidance, support, and expertise. This was a critical part of the process in completing this thesis. I would also like to thank Dr. Michael Hambourger, Dr. Brian Raichle, and Dr. Erick Bandala for their feedback, thoughtful questioning, laboratory training and space, and knowledge. In addition, I would like to particularly thank Dr. Erick Bandala for giving me the opportunity to go to the Universidad de las Américas Puebla to perform tests and more. He established the idea of using AOPs and the Fenton reaction at Appalachian State University. Without him, this thesis would not be possible. I would also like to acknowledge my parents, Terry and Tami Edge, for their support throughout my life. They have been available for help through my whole life, which has allowed me to be successful.

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CHAPTER 1: INTRODUCTION

Introduction

The water from salons is polluted with many types of chemicals. Two chemicals that are commonly found are surfactants and dyes, and the conventional process of treating wastewater is not effective at removing these contaminants. The specific pollutant that will be analyzed in this study is azo dye. Azo dyes are synthetic organic dyes and are used commonly in hair dye for their range of colors and their low cost (Morel & Christie, 2011; Scarpia, Nincia, Centinib, & Anselmib, 1998). There are a few methods that can be used to remove dye from wastewater. These methods include chemical treatment, oxidation, advanced oxidation processes (AOPs), and biological treatments. Previous studies show that oxidation and AOPs are effective ways to treat water polluted by azo dyes (Bandala, Peláez, García-López, Salgado, & Moeller, 2008; Bandala & Raichle, 2013; Bandala, Velasco, & Torres, 2008; Chacon, Leal, Sanchez, & Bandala, 2005). The effectiveness of oxidation processes will be examined in this study.

Oxidation is a loss of electrons from an atom and a common method for treating wastewater. There are different chemicals and methods used in oxidation which include chlorine, hydrogen peroxide, Fenton reaction, ozonation, electrochemical, and AOPs. The method of oxidation that will be studied will be the Fenton reaction. The Fenton reaction uses hydrogen peroxide as an oxidizing agent and iron as a catalyst. Studies have shown how effective the Fenton reaction is at degrading dye, but no studies were found that examine the treatment of hair salon wastewater. Relative dye concentrations will be determined using an ultraviolet–visible spectrometer.

Statement of the Problem

The particular application for which this study is examining the effective removal of dye with the Fenton reaction is the on-site treatment of hair salon greywater with a biological system for reuse in the facility's toilets. Preliminary tests of the system have shown it ineffective at removing dye from the greywater and yet removal of color is essential for reuse in toilet facilities. More generally, treating wastewater properly is one of the most important ways we can protect the environment. Wastewater can be filled with pollutants that need to be removed to prevent health and environmental problems. Wastewater from hair salons can contain hair dyes and surfactants. One of the most common types of dyes used are azo dyes (Gupta & Suhas, 2009).

The large amount of dyes that are introduced into the environment and the possible side effects of dyes shows there is a need to determine an effective method for removing them. The conventional methods for treating wastewater are ineffective for removing azo dyes. These dyes have been found to be harmful to people and the environment. For humans, they can act as carcinogens and mutagens. (Christie, 2007; Puvaneswari, Muthukrishnan, & Gunasekaran, 2006). For other organisms, they can impede plant growth and affect fish health as well (Chequer et al., 2013; Sun et al., 2006). The dye used in this study is a food dye that is safe to consume, but this study could be applicable to more harmful ones.

The Fenton reaction has been found to be effective at removing dyes (Bandala et al., 2008b; Bandala & Raichle, 2013; Chacon et al., 2005). The treated water from the Fenton reaction can have a significant amount of the toxins removed in addition to a reduction of chemical oxygen demand (COD; i.e., the amount of organic compounds in water) (Bandala, Peláez, 2008; Ertugay & Acar, 2013). For these reasons, oxidation processes seem to be a

promising method for treating salon wastewater, however there are concerns that the pH required for a successful Fenton reaction may detrimentally affect the proposed biological greywater treatment system.

Purpose of the Study

The purpose of this study is to analyze the degradation of azo dyes found in salon wastewater. It will look specifically at the removal of Allura red, a particular type of azo dye, using the Fenton process. The ultimate goal of this line of research is to find what conditions might be the most effective for removing common salon dyes from wastewater.

Research Questions

1. How do the amounts of ferrous sulfate and hydrogen peroxide affect the ability of the Fenton reaction to remove Allura red dye?
2. How does pH affect the Fenton reaction with the chemicals from Question 1?

Limitations of the Study

One limitation of this study is only one dye is analyzed. Results of this study may not reflect the effectiveness of the Fenton reaction to treat other compounds in salon wastewater. Salon wastewater could have other types of dyes which might degrade differently. Surfactants are common in salon water as well, and could change the ability of the Fenton process to remove dye by adding to the amount of organic compounds.

Significance of the Study

This study sought to determine the effectiveness of degrading azo dyes using the Fenton processes. This study may help show the effectiveness of Fenton reaction to remove the dyes from hair salon wastewater. The Fenton reaction, if shown effective, could be used in small-scale wastewater treatment facilities. Although this study focuses on a class of dyes found in salon

wastewater, these dyes are also in industrial wastewater. This study can add more evidence for the use of the Fenton reaction in the removal of these chemicals.

CHAPTER 2: REVIEW OF LITERATURE

Common Water Pollutants in Hair Salon Wastewater

Dyes

There are many types of dyes, but this study is focused on azo dyes. These dyes are used 0n nylon, wool, silk, modified acrylics, paper, leather, food, and in cosmetic or hair dyes. Azo dyes are synthetic organic dyes that contain nitrogen as an azo group (-N=N-) in their molecular structure. The N=N double bond is the key feature of an azo compound. The pi electrons of the azo group can delocalize across adjacent conjugated networks, making the azo linkage a favored method of coupling aromatic ring systems for dye synthesis. By extending the conjugated network, the azo linkage can lower the excitation energy such that the product molecule absorbs visible light and is a useful dye (Smith & March, 2007). These dyes can be produced in a wide range of colors with relative synthetic ease. For these reasons, azo dyes are widely used (Gupta & Suhas, 2009). Although azo dyes are found largely in the textile industry, this study looked at dyes used in cosmetics. The dye that was analyzed waAllura red AC. The molecular structure of Allura red AC can be found in Figure 1. This dye is typically used in food coloring but is similar to hair dye. It was chosen for convenience and for health reasons.

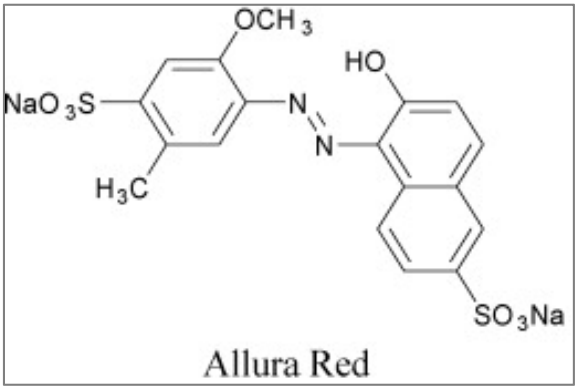

Figure 1. Allura red AC (Salem, Al-Ghonemiy, & Zaki, 2009, p. 60)

Surfactants

A surfactant is a chemical that is both hydrophilic and lipophilic, and the types of surfactants are differentiated by ionic characterization. There are four types: anionic, non-ionic, cationic, and amphoteric. Surfactants are used frequently in cosmetics. Their main uses in cosmetics include cleaning, emulsification, solubilization, and conditioning. The amount of surfactants in wastewater is unclear, but traditional methods and AOPs can be used to remove surfactants (Adak, Bandyopadhyay, & Pal, 2005). This study analyzed the process to remove azo dyes from salon wastewater, but the process may also be used to remove surfactants.

Effects of Water Pollutants Found in Salon Wastewater

When using surfactants and dyes there can be many side effects. Both of these pollutants are used frequently. Because the traditional methods for removing these substances are ineffective, the effects of these pollutants need to be understood (El-Gohary, Tawfik, & Mahmoud, 2010). It is understood that these pollutants do not easily biodegrade, and wastewaters containing surfactants and dyes typically have elevated levels of COD and total organic carbon (TOC) (Chequer et al., 2013; Slokara, Zupanb, & Marechal, 1999). COD and

TOC are a measure of the amount of organic matter in water. High levels can cause bacteria to consume oxygen present in water, leaving less for aquatic animals (Nathanson, 2008).

Surfactants are perhaps the least concerning. Surfactants are not considered to be toxic to humans, but some mammals have been found to be acutely affected (Marin Municipal Water District, 2010). According to the Marin Municipal District (2010), "in general, aquatic organisms are more susceptible to adverse effects from surfactants than terrestrial organisms because surfactants can adsorb to biological membranes (skin, gills) and disrupt biological functions" (p. 10). It has also been reported that nonylphenol, a surfactant, can change breeding patterns in fish. Low doses of nonylphenol will increase male breeding behavior, whereas high doses hinder their sexual behavior (Schoenfuss et al., 2008). The toxicity of the surfactant has been found to increase with the effective length of the hydrophobic chain (Kosswig, 2000).

Dyes are of more concern, because they affect mammals, plants, and aquatic organisms. With 3000 tons of azo dyes being certified for use in foods by the US Food and Drug Administration in 1991, they may pose a threat to the environment (Puvaneswari et al., 2006). Some countries, including Germany and the Netherlands, have created laws banning azo dyes, and other European countries such as Sweden, France, Denmark, and the European Union are creating legislation for regulating and prohibiting use of azo dyes (Christie, 2007). It is generally accepted that dyes may be cleaved to create mutagenic and carcinogenic aromatic amines (Chequer et al., 2013; Puvaneswari et al., 2006; The Scientific Committee on Cosmetic Products and Non-Food, 2002); however, it has been found that aromatic amines present a low level of genotoxic potential (Jung, Steinle, & Anliker, 1992).

Azo dyes can negatively affect multiple parts of the environment. The use of hair dye, in general, has been linked to leukemia, lymphoma, human bladder cancer, splenic sarcomas, skin and eye irritation and sensitivity, hepatocarcinomas, and liver nodules (Cantor et al., 1988). In

animals, dyes have also been found to be carcinogenic and tumorigenic (Christie, 2007; Hatch & Maibach, 1999; Puvaneswari et al., 2006; Rai et al., 2005). The effect of dye can be indirectly damaging to humans. Compounds from dyes can be ingested by aquatic organisms and then harm humans through the food chain. The azo dye HC Orange No. 1 has been found to cause liver damage to goldfish from oxidative stress and injury to the cellular membrane system (Sun et al., 2006). The Biological Oxygen Demand (BOD), COD, and color changes associated with dye pollution have been found to negatively affect the biological cycles of bodies of water, changing the processes of photosynthesis and oxygenation (Chequer et al., 2013). In addition, azo dyes can harm plant's germination percentage, seedling survival and height, and chlorophyll contents (Puvaneswari et al., 2006).

Water Remediation Processes

There are many different processes for removing dyes from wastewater. These processes include filtration, chemical, oxidation, AOPs, and biological treatments. These will be discussed further in the following paragraphs.

Filtration

Filtration is a common method for physically treating wastewaters. In typical municipal wastewater treatment facilities there are a variety of screening systems; however, these systems are not effective at removing dyes. Dye removal requires advanced systems such as ultrafiltration, nanofiltration, and reverse osmosis, all of which involve forcing water through membranes that prevent contaminants to pass (Cheremisinof, 2002). These processes are very effective at removing dye from wastewater; however, they also consume energy, require high working pressures, and generate waste from membrane use (Gupta & Suhas, 2009).

Chemical

Chemical processes are generally used to enhance physical processes such as sedimentation. Chemical processes include mixing with coagulating or flocculating agents which can be used to remove metals from typical wastewater (Shi, Li, Wang, Feng, & Tang, 2007). The typical phases of chemical processes include adding the chemicals, rapid mixing to create a homogeneous solution, slow mixing to create flocculation, and then filtration to remove pollutants. Chemical processes remove certain dyes but are ineffective at removing azo dyes. Another problem that is found with chemical processes is they produce large quantities of sludge (Lee, Choi, Thiruvenkatachari, Shim, & Moo, 2006).

Oxidation

Chemical oxidation involves the use of oxidizing agents. Oxidative processes are the most commonly used to remove dye, and they generally involve pH control (Gupta & Suhas, 2009). Chlorine is typically used as a disinfectant or bleaching chemical in wastewater and industrial facilities, but can also be used in the oxidation of dyes. Chlorine oxidation is most effective with water soluble dyes, including azo dyes. The cost and the efficiency can be improved with the use of chlorine gas, but can also result in negative side effects, such as an increase of organic halogens in the treated water and corrosion in metal vessels (Gupta & Suhas, 2009).

Another oxidizing agent is hydrogen peroxide. As with chlorine, hydrogen peroxide is used frequently in bleaching (Hage & Lienke, 2006). Although hydrogen peroxide can be used alone in the oxidation of dye, the process can be improved by adding iron as a catalyst. This is called the Fenton reaction and is not completely understood. Currently, there are two theories describing how the Fenton reaction occurs (Dunford, 2002). The first theory incorporates radical chemistry. During the oxidation process, radicals are produced when iron(II) is oxidized to

iron(III). Equations 1, 2, and 4 show the oxidation reactions. Then iron(III) is reduced back to iron(II), which is seen in Equation 5. Equation 3 shows the reaction of hydrogen peroxide and a hydroxyl radical, producing water and another radical. The radicals produced degrade organic compounds such as dyes by removing an electron and creating another radical. Radical chemistry will continue until radicals interact with other radicals terminating the process. The second theory of Fenton chemistry doesn't involve radical theory. Instead, it is only the reactions with hydrogen peroxide and iron that degrade organic compounds (Kremer, 1999). The radical theory is the most accepted (Dunford, 2002).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + HO^- \quad (1)$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + HO^- \quad (2)$$

$${}^{\cdot}OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \quad (3)$$

$$HO_2^{\cdot} + Fe^{2+} \rightarrow Fe^{3+} + HO_2^- \quad (4)$$

$$HO_2^{\cdot} + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \quad (5)$$

There are many factors that can affect the effectiveness of the Fenton reaction at removing dye (Gupta & Suhas, 2009; Araujo, Yokoyama, Teixeira, & Campos, 2011; Bandala, Peláez, 2008). Factors that change the effectiveness of the Fenton reaction include the concentration of each reactant (iron, hydrogen peroxide, and organic compounds), temperature, and pH levels. The pH changes the reaction by changing how iron behaves (Duesterberg, Mylon, & Waite, 2008; Machulek et al., 2012). Different pH levels will either cause iron to precipitate or stay in solution. Figure 2 shows how iron(II) and iron(III) exist as pH levels change from 0 to 14 and as the electrochemical potential changes from -4 to 3. At the electrochemical potential of

0.77V, $Fe^{3+}(aq)$ will reduce to $Fe^{2+}(aq)$ below a pH of about 2. The ions $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ may precipitate from solution and create FeO(OH)(s) in the pH range of 1.3 to 6. The ion $Fe^{2+}(aq)$ will also precipitate at a pH of 6.0 with the formation of $Fe(OH)_2(s)$. If iron(II) precipitates, the equations 1, 2, and 3 will not occur and reduce the effectiveness of the Fenton reaction (Bandala, Peláez, 2008; Cheng, Ma, Li, Huang, & Zhao, 2004; Duesterberg et al., 2008; Dunford, 2002).

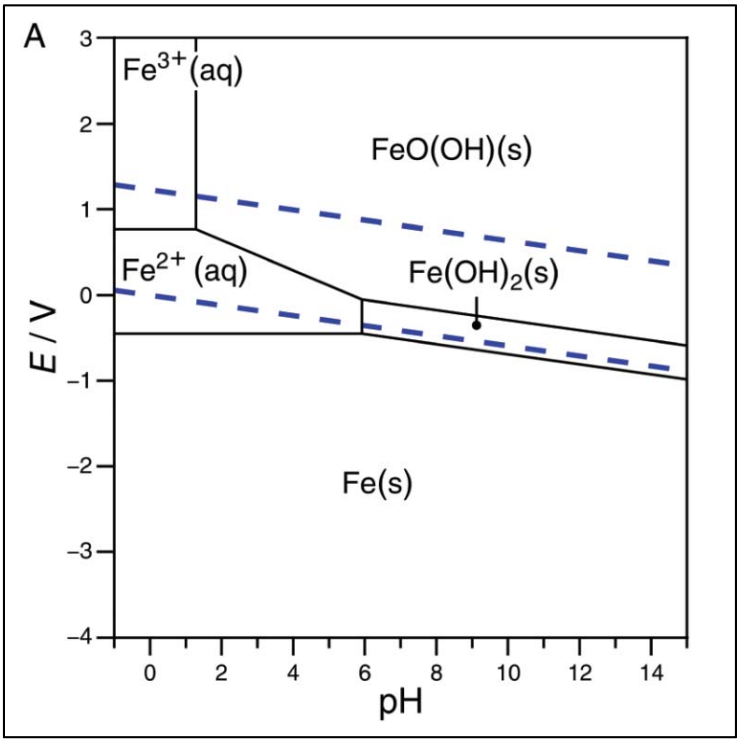

Figure 2. Iron Pourbaix Diagram (Pesterfield, Maddox, Crocker, & Schweitzer, 2012, p. 897)

Ozonation is another oxidation process used in wastewater treatment. Ozone is a reactive chemical and, therefore, has many uses in treating water. It can improve biological and flocculation processes, remove metals, and degrade pollutants (Paraskeva & Graham, 2002). One of the pollutants it can degrade is azo dyes. Ozonation has also been found to be effective at lowering COD. Some of the drawbacks to ozonation are cost and ozone's short half-life. A short half-life will require constant ozonation, making the process expensive (Robinson, McMullan, Marchant, & Nigam, 2001).

Electrochemical methodologies, a method of placing an anode and a cathode in the water, have been used for both dye removal and disinfection of water. When a current is applied, electrolysis occurs and allows oxidation and reduction reactions to take place. Electrochemical methodologies have been found to be effective at removing azo dyes. They can also aid in the reduction of COD (Doğan & Türkdemir, 2015; Faouzia, Nasrb, & Abdellatifa, 2007). The drawbacks of electrochemical methodologies include the cost, sludge generation, and other pollution. Electrochemical methodologies use energy for the electrolysis to occur. Some of the pollution from electrochemical methodologies includes the addition of chlorinated organics and heavy metals (Gupta & Suhas, 2009).

Advanced Oxidative Processes

AOPs involve using multiple types of oxidation processes to increase the effectiveness of removing pollutants. These processes take advantage of free radicals, particularly hydroxyl radicals, to oxidize and degrade contaminants in wastewater. AOPs are known to oxidize organic pollutants into CO_2 and are attractive due to their ability to use renewable resources such as the sun as a source of UV photolysis (Bandala & Raichle, 2013). The techniques used in AOPs include photocatalysis and sonolysis. There are also various processes involving ozone and hydrogen peroxide with UV light (Gupta & Suhas, 2009).

Photocatalysis is a method where light excites electrons of the catalyst and hydroxyl radicals are formed. Photocatalysis has been found to remove pesticides, dyes, surfactants, and bacteria. One of the types of photocatalytic methods is homogeneous which is where the reactants and the photocatalysts are in the same phase. A commonly used homogenous method is the photo-Fenton reaction. The photo-Fenton process increases the efficiency of the Fenton reaction process with the use of UV-light (Bandala, Peláez, 2008). In a study by Chacon, Leal, Sanchez, and Bandala (2005), the azo-dye orange 24 was removed using the photo-Fenton

reaction and solar energy. They were able to achieve between 85-95% removal of the dye. The other type of photocatalysis is heterogeneous which is where the reactants are not in the same phase. Heterogeneous photocatalysis can include a solid substrate of the photocatalysts where the solution of hydrogen peroxide and organic substances can interact with it (Bandala & Raichle, 2013; Gupta & Suhas, 2009).

Sonolysis is a process that uses ultrasonic waves to degrade dyes in wastewater. The process works by creating radicals from violent cavitation events, and it has been found that factors in the process include ultrasound power and total solution volume. The method has been found to remove azo dyes, but can be expensive (Gupta & Suhas, 2009).

Biological

Biological treatment is the use of organisms, namely bacteria and fungi, to remove pollutants such as dye from wastewater. There are three different biological treatment which are aerobic, anaerobic, or a combination of the two (Gupta & Suhas, 2009). Aerobic treatment involves the use of oxygen and has been found to be effective at removing a number of non-azo dyes (Sani & Banerjee, 1999). Fungi have been found to degrade some azo dyes but cause biodegradation causing maintenance of the system. Anaerobic treatment does not require oxygen, and a variety of synthetic dyes have been found to be biodegradable; however, azo dyes have been determined to be nonbiodegradable (Rai et al., 2005). In addition, anaerobic treatment does not require aeration unlike aerobic which reduces the cost. The drawbacks to anaerobic treatment include insufficient BOD removal and dyes are not degraded (Delee, O'Neill, Hawkes, & Pinheiro, 1998). In a combination of aerobic and anaerobic treatment, studies have shown that azo dyes can be removed from wastewater with the use of aerobic posttreatment of the system; however, the cost of posttreatment increases the cost of the system. Biological treatment is a cheap method to treat wastewater; however, it cannot treat all types of dyes, namely azo dyes.

Other negative aspects to biological treatment include limitations to the design and operational feasibility and the fact that it consumes space and treatment can take a long time (Gupta & Suhas, 2009).

CHAPTER 3: RESEARCH METHODOLOGY

This was an experimental study examining the effectiveness of the Fenton reaction at degrading dye. Three different experiments were conducted. All three involved measuring the percent of dye remaining by taking absorbance and kinetics traces. This was accomplished by using a UV-vis spectrophotometer to record dye absorbance in a one-centimeter pathlength cuvette. The first, preliminary, experiment looked at the degradation of the dye without stirring while measuring with the UV-vis, the second experiment incorporated stirring, and the third had varying pH levels. All experiments consisted of tests using Allura red dye, ferrous sulfate, and hydrogen peroxide. The third method used sodium citrate and sodium phosphate as buffers to control pH levels.

Data Collection Instrumentation and Chemicals

Below is a list of the data collection instrumentation and chemicals used in this study:

- UV-Vis: Shimadzu Corp. Kyoto, Japan, model UV-2401PC
- pH meter: Orion Instruments Baton Rouge, LA, model 710A
- Cuvette Spinette: Starna Atascadero, CA, model SCS1.11
- Hydrogen Peroxide (35%), CAS: 7722-84-1 manufactured by Fisher Chemical Pittsburgh, PA
- Allura Red AC dye, CAS: 25956-17-6 manufactured by Sigma-Aldrich St. Louis, MO
- Ferrous Sulfate, CAS: 7782-63-0 manufactured by J.T. Baker Center Valley, PA

- Deionized water
- Sodium Phosphate, CAS: 7558-80-7 manufactured by Sigma-Aldrich St. Louis, MO
- Sodium Citrate, CAS: 68-04-2 manufactured by Sigma-Aldrich St. Louis, MO

Data Collection Procedures

Preliminary Tests

The purpose of the preliminary tests was to identify likely conditions for effective dye degradation using the Fenton reaction. These preliminary tests included preparing 3-milliliter samples with three different concentrations each of ferrous sulfate, Allura red dye, and hydrogen peroxide. The concentrations are referred to as low, moderate, and high (Table 1). High concentrations were used to ensure the reaction occurred and dye was removed. The samples were prepared using stock solutions of each component. The concentrations of the stock solutions were 5.5 mM ferrous sulfate, 0.1 mM stock dye, and 11.64 M hydrogen peroxide. These solutions were diluted to the testing concentrations with deionized (DI) water. A spectrometer absorbance trace of the Allura red for each of the concentrations can be seen in Figure 3. An outline of a trial of tests can be found in Table 2 and Table 3. There were a total of 45 tests, 18 control tests, and 27 non-control tests. A step-by-step description of a testing procedure follows.

1. Prepare stock solutions.
    a. Ferrous Sulfate – 5.5 mM solution with DI water and HCl. The pH was adjusted to approximately 2 or 3 using hydrochloric acid. The pH was measured with a litmus test.
    b. Dye stock – 0.1mM solution with in DI water
    c. Hydrogen peroxide – 35% H_2O_2 solution (11.64 M)

2. Calibrate the UV-vis spectrometer to measure absorbance from 400 to 800 nm and the kinetics at 501 nm. Set the sample interval to 0.1 seconds.
3. Fill a cuvette with only DI water, and complete a baseline absorbance with the UV-vis.
4. Fill a 3 mL cuvette with the correct volumes of ferrous sulfate, Allura red dye, and DI water using a pipette to dilute each reagent to its testing concentration.
5. Place cuvette in the UV-vis.
6. Take a measurement of the absorbance of the sample.
7. Start a kinetic trace of the sample that lasted 120 seconds. Approximately 30 seconds through the kinetic trace place hydrogen peroxide using a pipette into the cuvette.
8. Take a measurement of the absorbance after the kinetic trace.

Table 1. *Concentrations of Iron, Hydrogen Peroxide, and Dye Used*

	Low	**Moderate**	**High**
Ferrous Sulfate (mM)	0.11	1.1	2.2
Hydrogen Peroxide (mM)	39	172	339
Allura Red Dye (mM)	10	20	50

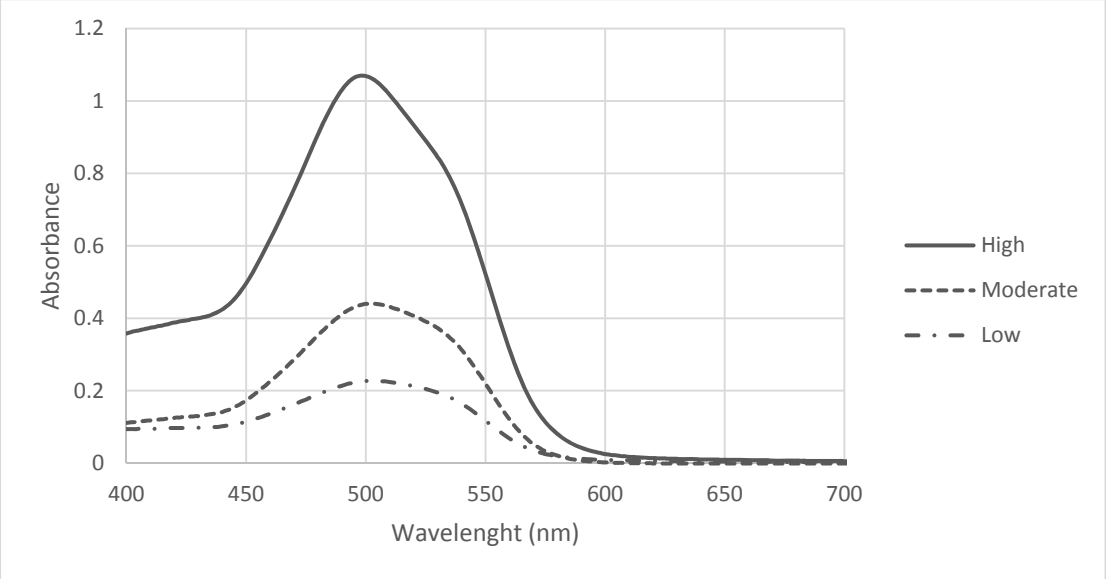

Figure 3. Absorbance of Allura red with high, moderate, and low concentrations.

Table 2. *Outline of Test Concentrations*

Test #	Iron (mM)	H_2O_2 (mM)	Dye (mM)
1	1.1	39	20
2	1.1	339	10
3	2.2	339	50
4	2.2	172	10
5	1.1	172	20
6	1.1	39	10
7	2.2	39	10
8	2.2	172	50
9	1.1	39	50
10	2.2	339	10
11	0.11	339	20
12	0.11	39	10
13	1.1	339	20
14	0.11	39	20
15	0.11	172	20
16	1.1	172	50
17	0.11	39	50
18	0.11	339	50
19	2.2	39	50
20	0.11	172	10
21	0.11	172	50
22	1.1	172	10
23	2.2	339	20
24	2.2	39	20
25	0.11	339	10
26	1.1	339	50
27	2.2	172	20

Table 3. *Outline of Control Test Concentrations*

Test #	Iron (mM)	H_2O_2 (mM)	Dye (mM)
1	1.1	0	20
2	0.11	0	10
3	1.1	0	10
4	2.2	0	20
5	2.2	0	50
6	0.11	0	50
7	2.2	0	10
8	1.1	0	50
9	0.11	0	20
10	0	339	10
11	0	172	50
12	0	339	50
13	0	39	50
14	0	39	10
15	0	172	20
16	0	39	20
17	0	172	10
18	0	339	20

Stirring Effects

The second experiment was very similar to the previous method and incorporated stirring the solution in the cuvette while measurements were recorded. The experiment was done using a Starna Spinette. The concentrations of the reagents used for stirring were initially chosen to be the concentrations found in method one. However, the concentrations of hydrogen peroxide were further diluted to 4.04×10^{-1} mM to reduce systematic uncertainties in the UV-vis spectrometer due to bubble formation. A serial dilution was made of both of the reagents and tested. The concentrations for each test that was performed can be seen in Table 4. During these trials, measurements were made at one-second intervals for 600 seconds. All of the tests only included one trial per condition. This was done because there was a limited amount of time to complete this study. To understand the possible uncertainties to these conditions, a set of replicates of the concentrations iron 1.1×10^{-1} mM, hydrogen peroxide 4.04×10^{-2} mM, and dye 20 mM were

conducted to determine the reproducibility and the possible standard deviation of the tests in this section.

Table 4. *Stirring Effects Test Summary*

	Concentrations of reagents		
	Iron (mM)	**H_2O_2 (mM)**	**Dye (mM)**
Serial Trial 1	$1.1x10^{-1}$	$4.04x10^{-2}$	20
	$1.1x10^{-2}$		
	$1.1x10^{-3}$		
	$1.1x10^{-4}$		
	$1.1x10^{-5}$		
Serial Trial 2	5.4×10^{-1}	$4.04x10^{-1}$	20
		$4.04x10^{-2}$	
		$4.04x10^{-3}$	
		$4.04x10^{-4}$	
		$4.04x10^{-5}$	
Serial Trial 3	$1.1x10^{-1}$	$4.04x10^{-1}$	20
		$4.04x10^{-2}$	
		$4.04x10^{-3}$	
		$4.04x10^{-4}$	
		$4.04x10^{-5}$	
Serial Trial 4	$1.1x10^{-1}$	$4.04x10^{-1}$	50
		$4.04x10^{-2}$	
		$4.04x10^{-3}$	
		$4.04x10^{-4}$	
		$4.04x10^{-5}$	

pH and Buffer Effects

This experiment examined how pH affected the ability of the Fenton reaction to remove dye and was very similar to the second method, except that phosphate 25mM and citrate 25mM buffers were used in the preparation of the stock solutions. Three different conditions to control pH were used in this experiment: (1) incorporating a mix of the pH buffers phosphate and citrate into the DI water, (2) incorporating only phosphate buffer in the DI water, and (3) incorporating no buffer in the DI water. All of the pH conditions were adjusted to pH 2, 5, and 7 using both

hydrochloric acid and sodium bicarbonate. Once the stock solutions were created, each test followed the same procedure as the stirring experiment with the additional step where a litmus test was performed after each test. Reagent concentrations chosen were the best performing concentrations in the stirring effects section (iron 0.11mM, hydrogen peroxide 0.0404mM, and dye 20mM).

Data Analysis Procedures

All of the experiments were analyzed by comparing the percentage of dye remaining at the end of the reaction. The end of the reaction was determined to be when the degradation curve appeared to stop removing dye. All raw absorption measurements from kinetic traces were converted to a percentage of the initial dye concentration which was done by dividing each data point by the first measured point in the kinetic trace and multiplying by 100% (Equation 6). The multiple trials for each set of concentrations are represented as the averages and the standard deviation of the three trials.

$$\frac{Absorbance}{Initial\ Absorbance}\ x\ 100\% = Percentage\ of\ Dye\ Remaing \quad (6)$$

CHAPTER 4: RESULTS

Preliminary Tests

Out of all of the tests, only eight specific test conditions produced results with acceptable uncertainties. The threshold for acceptable uncertainties was based on the standard deviation of the amount of dye remaining and the appearances of the degradation curve. If any test had a standard deviation above 10% and the degradation curves did not appear similar to the others, it was an unacceptable result. An example of a test with unacceptable uncertainties can be seen in Figure 4. The controls showed that both hydrogen peroxide and iron do not independently degrade dye. Each preliminary test was analyzed by looking at the average and the standard deviation of the three replicate trials.

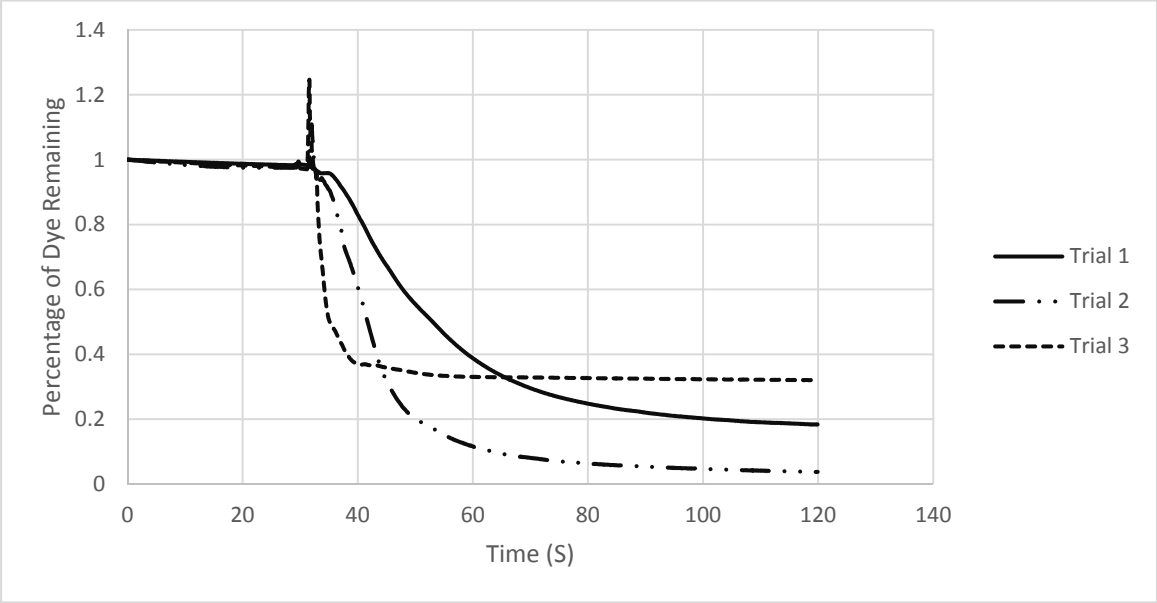

Figure 4. Unacceptable test results with concentrations low iron, low hydrogen peroxide, low dye.

Table 5 shows the tests where iron concentration was moderate while dye and hydrogen peroxide were high, low, or moderate. For these set of conditions, moderate concentrations of hydrogen peroxide performed better than high concentrations, but dye concentration does not seem to change the amount of dye remaining.

Table 5. *Final Dye Remaining with Moderate Concentration of Iron and Concentrations of Dye and Hydrogen Peroxide were High, Moderate, and Low*

H_2O_2	Dye	Average percent of dye remaining
High	**Low**	28.3±5.6%
High	**Moderate**	26.3±3.7%
High	**High**	20.5±7.5%
Moderate	**High**	16.5±2.9%
Moderate	**Moderate**	16.4±5.3%

Table 6 shows the tests where hydrogen peroxide concentration was moderate while iron and dye were high, moderate, and low. For these set of conditions, higher concentrations of iron are more effective at removing dye. Table 6 also supports the pattern found in Table 5 where the amount of dye does not affect the percentage of dye remaining.

Table 6. *Final Dye Remaining with Moderate Concentration of Hydrogen Peroxide and Concentrations of Dye and Iron were High, Moderate, and Low*

Iron	Dye	Average percent of dye remaining
Low	**High**	51.6%±4.3%
Moderate	**High**	16.5%±2.9%
Moderate	**Moderate**	16.4%±5.3%
High	**High**	9.3%±1.2%

Table 7 shows the tests where dye concentration was moderate while iron and hydrogen peroxide were high and moderate. If the results from Tables 5 and 6 are compared to the results in Table 7, it seems hydrogen peroxide concentration might have a larger effect on the Fenton

reaction. Table 5 shows hydrogen peroxide is more effective in lower concentrations, and Table 6 shows iron is more effective at higher concentrations. In Table 7, the highest concentrations of iron and peroxide were the least effective, and the most effective were moderate iron and hydrogen peroxide. If iron had a larger effect on the reaction, the highest iron concentration would not be the worst condition in Table 7.

Table 7. *Final Dye Remaining with Moderate Concentration of Dye and High and Moderate Concentrations of Iron and Hydrogen Peroxide*

Iron	H_2O_2	Average percent of dye remaining
High	**High**	32.7±6.8%
Moderate	**High**	26.3±3.7%
Moderate	**Moderate**	16.4±5.3%

The purpose of the preliminary section was not to optimize the concentrations of the reagents to remove the most amount of dye but to find conditions that could be used for further experimentation. The conditions that were chosen were moderate iron, high peroxide, and moderate dye which had 26.3±3.7% dye remaining at the end of the test. There were other conditions that removed more dye, but the chosen condition would allow noticeable improvements in dye removal to be observed.

Stirring Effects

The initial tests with stirring of the concentrations of moderate iron, high hydrogen peroxide, and moderate dye had large uncertainties likely due to excessive bubble formation. Iron and hydrogen peroxide were diluted to lower the production of bubbles. Hydrogen peroxide was lowered to similar concentrations of iron. These concentrations of iron and hydrogen peroxide have been found to effectively remove organic matter in other studies (Chacon et al., 2005; Neyens & Baeyens, 2003). Trials with lowered concentrations had much slower reactions

rates. Absorption was recorded every second for 600 seconds to compensate for the slower reaction rates. Some of the tests seemed to be complete by about the 300 second mark. Recording was occasionally stopped around 300 seconds into the tests to save time.

Figure 5 shows how the bubbles affected the tests, and how reducing the concentration of hydrogen peroxide improves reading the dye degradation. The bubbles cause random spikes and an unsteady degradation.

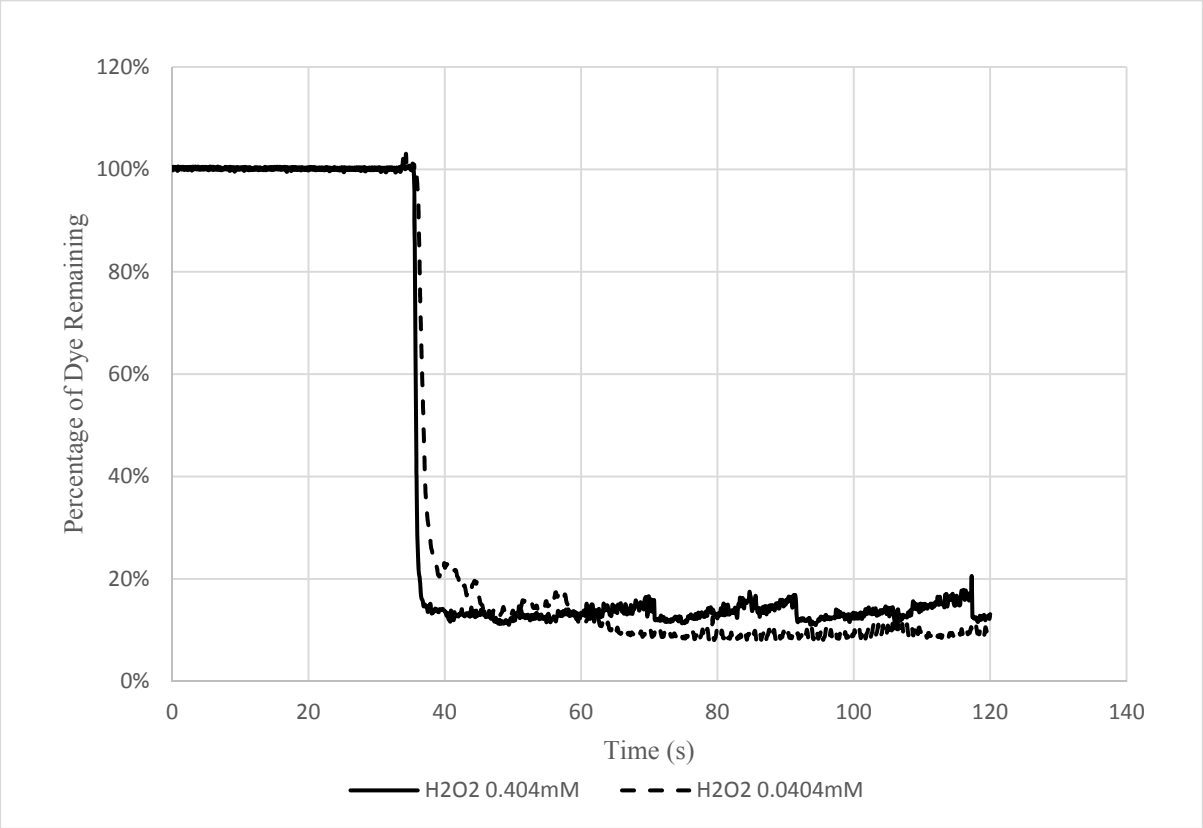

Figure 5. H_2O_2 concentrations of 4.04 x 10^{-1} mM and 4.04 x 10^{-2} mM with iron and dye concentrations moderate.

Six replicates of the test condition hydrogen peroxide 4.04 x 10^{-2} mM, iron low, and dye moderate were completed. The results of the replicate sampling can be seen in Figure 6 and Table 8. The replication of this condition had a standard deviation of approximately 2.3% for six replicates. The other stirring tests did not use replicates. Due to the excellent replication shown

in Figure 6 and Table 8, it was assumed that each test would have an approximate standard deviation of 2%.

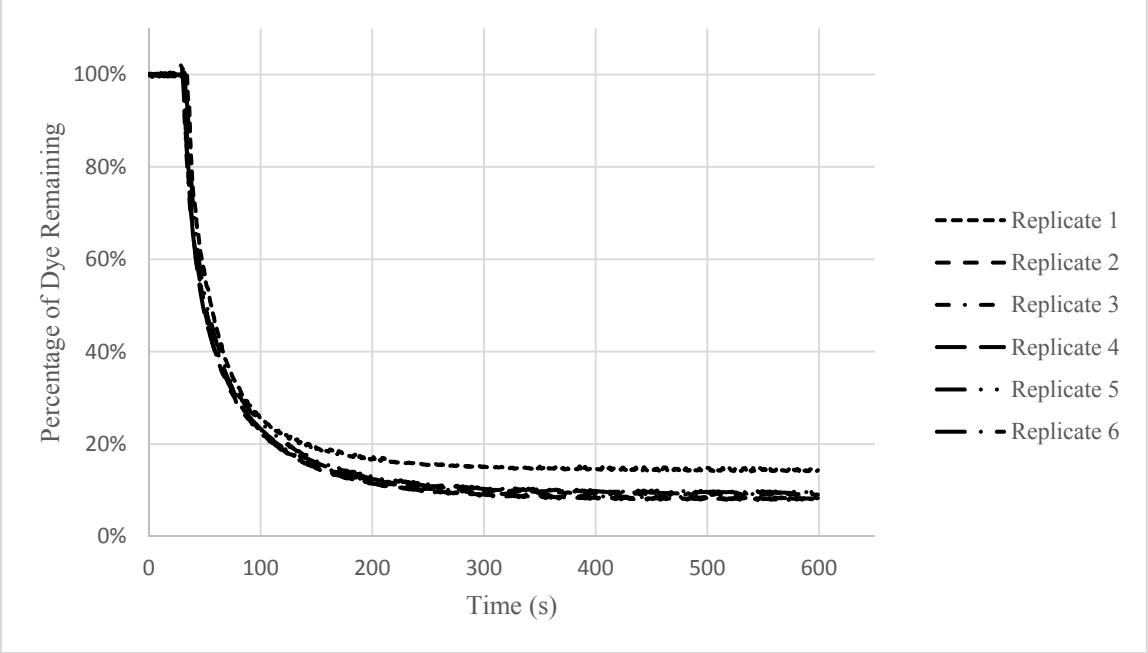

Figure 6. Replications of H_2O_2 4.04 x 10^{-2} mM, Iron 1.1 x 10^{-1} mM, Dye 20mM.

Table 8. *Replications of H_2O_2 4.04 x 10^{-2} mM, Iron 1.1 x 10^{-1} mM, Dye 20mM*

Test	Percent of dye remaining
Replicate 1	14.4%
Replicate 2	9.1%
Replicate 3	8.3%
Replicate 4	8.1%
Replicate 5	9.4%
Replicate 6	9.7%
Mean	9.8%
Standard Deviation	2.3%

Figures 7 and 8 show how iron affected the reaction and the limit at which it stopped being effective in the Fenton reaction. Any iron concentration below 1.1 x 10^{-1} mM, which was the

lowest iron concentration used in preliminary tests, will likely not provide effective conditions to remove dye. The concentration of 1.1 x 10^{-1} mM had 11% of dye remaining. Other studies with the Fenton reaction have found the best conditions result in near 10% of dye remaining (Bandala, Peláez, 2008; Chacon et al., 2005). The iron concentration could be near saturating the reaction at the concentration of 1.1 x 10^{-1} mM.

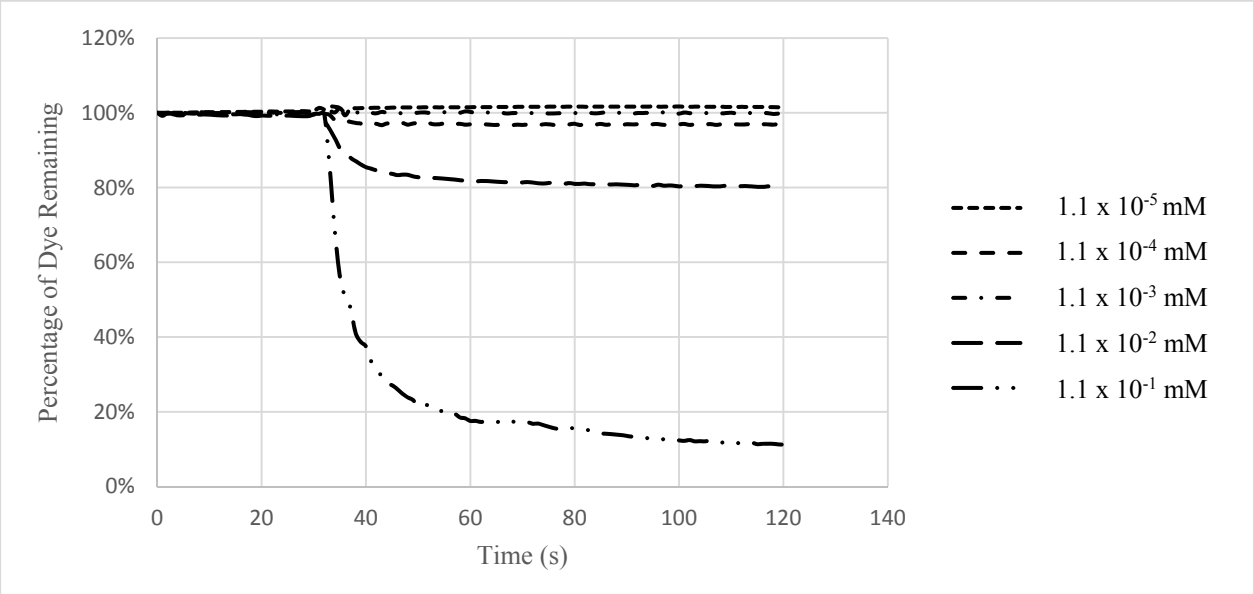

Figure 7. Varying iron concentrations from 1.1 x 10^{-1} mM to 1.1 x 10^{-5} mM with H_2O_2 concentrations of 0.0404 mM and dye 20 mM.

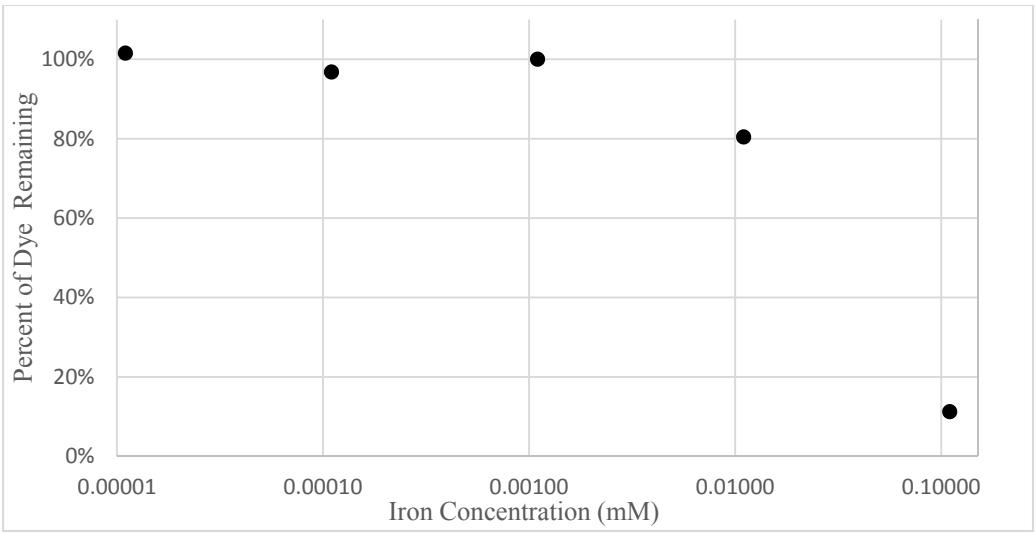

Figure 8. Percentage of dye at the end of tests with varying iron from 1.1 x 10^{-1} mM to 1.1 x 10^{-5} mM, H_2O_2 0.0404mM, and dye 20mM.

Figure 9 displays dye removal with varying concentrations of hydrogen peroxide with iron and dye concentrations at 5.4 x 10^{-1} mM and 20mM. The iron concentration is halfway between the moderate and low concentrations, and the dye is the moderate concentration. Although 4.04 x 10^{-2} mM had a similar amount of dye remaining as 4.04 x 10^{-1} mM, the degradation curve of 4.04 x 10^{-2} mM seems to have been slower. The condition best at degrading dye in Figure 9 removed 7%.

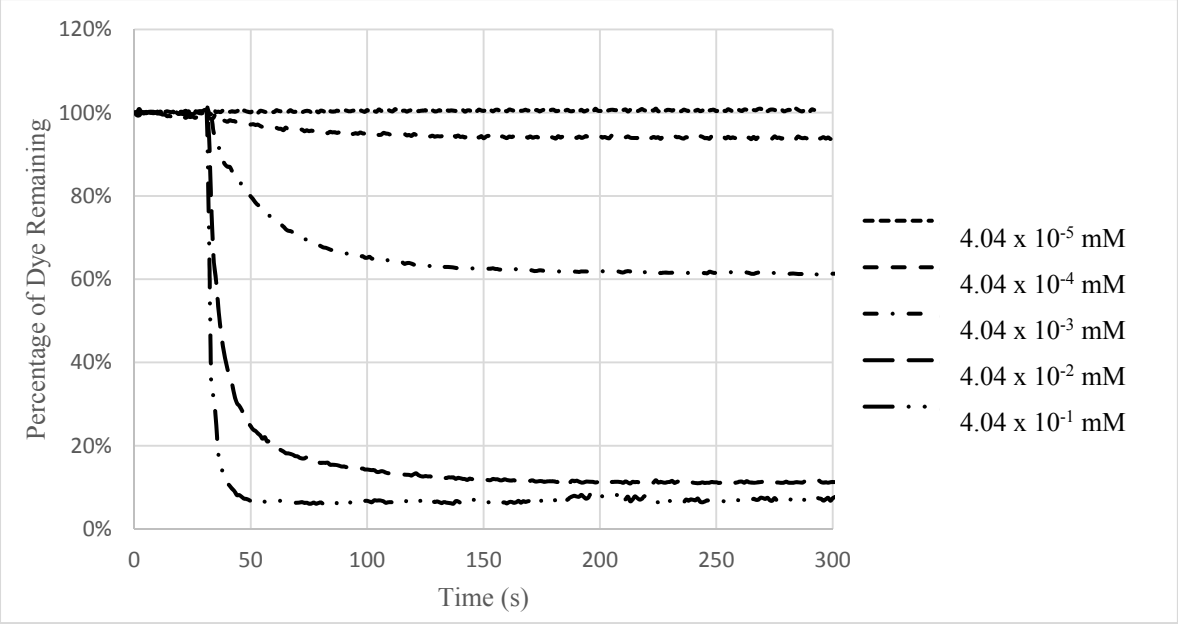

Figure 9. Varying H_2O_2 concentrations from 4.04 x 10^{-1} mM to 4.04 x 10^{-5} mM with iron and dye concentrations as 5.4 x 10^{-1} mM and dye 20 mM.

Figure 10 displays the dye concentrations for hydrogen peroxide with low iron and moderate dye. As with the previous test where hydrogen peroxide was varied (Figure 9), the degradation curves of the two highest concentrations were the most effective at degrading dye.

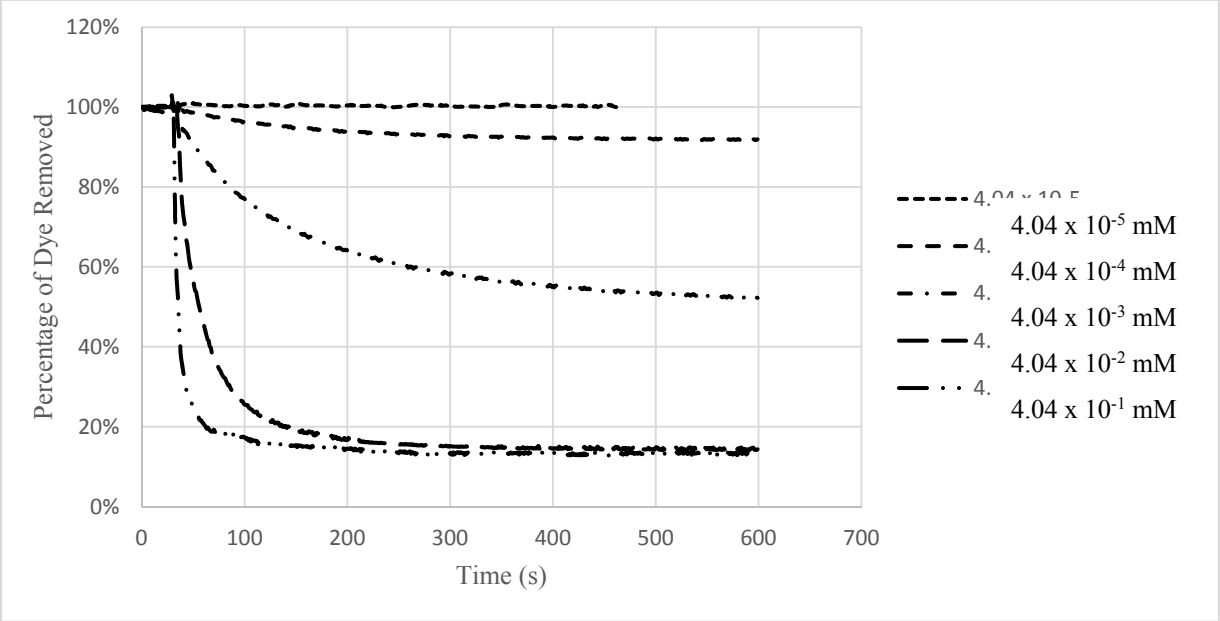

Figure 10. Varying H_2O_2 concentrations from 0.404 mM to 4.04 x 10^{-5} mM with iron and dye concentrations at 1.1 x 10^{-1} mM and Dye 20 mM.

Figure 11 shows how dye concentration changes the tests shown in Figure 10. The dye was increased from 20 mM (moderate) to 50 mM (high). Increasing dye concentrations slowed down the degradation of the dye. If one looks at concentrations 4.04 x 10^{-1} mM, 4.04 x 10^{-2} mM, and 4.04 x 10^{-3} mM in Figure 11, the degradation curve had not finished degrading dye by the 600th second. A statement on the remaining percentage of dye at the end of the reaction cannot be made. However, if the reaction was allowed to complete, it would likely not be substantially lower.

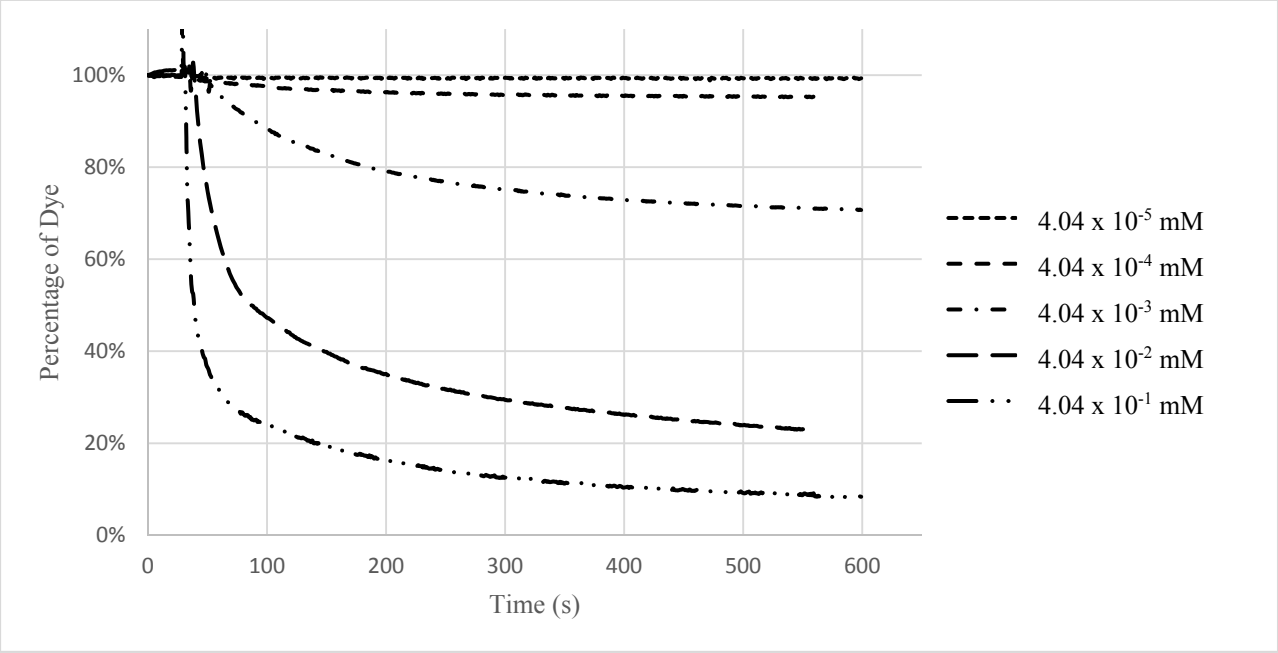

Figure 11. Varying H_2O_2 from 4.04 x 10^{-1} mM to 4.04 x 10^{-5} mM with Iron 1.1 x 10^{-1} mM and Dye 50 mM.

Figure 12 summarizes the amount of dye remaining from Figures 9, 10, and 11. It should be noted that data points from the tests iron 1.1 x 10^{-1} mM and dye 50 mM (Figure 11) do not represent the amount of dye remaining at the end of the reaction but the amount of dye remaining near the end of the reaction. These data points would likely not be much lower than they appear in Figure 12. For all cases, the two lowest concentrations of hydrogen peroxide were the worst at removing dye. The best concentrations of hydrogen peroxide for all three tests were 4.04 x 10^{-1} mM and 4.04 x 10^{-2} mM with 4.04 x 10^{-1} mM being slightly better. The graph shows that at low concentrations, as hydrogen peroxide was increased the more effective it was at removing dye, but tests performed in the preliminary section showed that much higher concentrations performed worse. The best conditions with stirring had approximately 10% dye remaining, but the same conditions with a hydrogen peroxide concentration of 339 mM hade 28.3±5.6% dye remaining (Table 5).

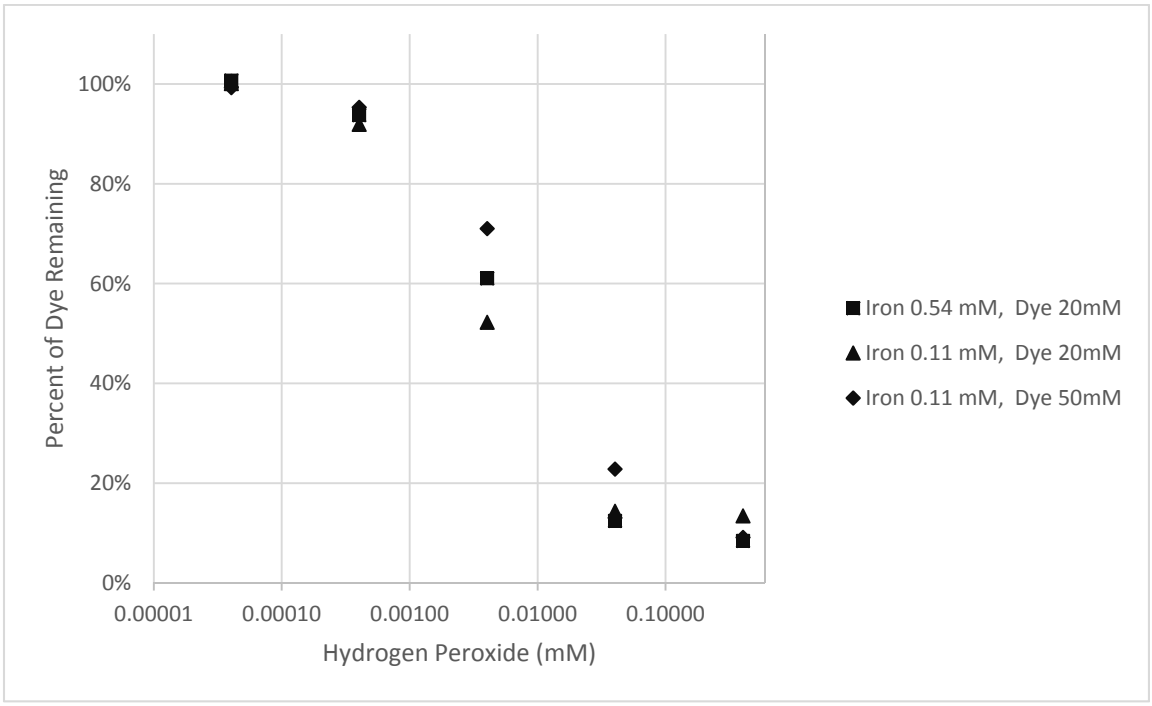

Figure 12. Summary of dye remaining where H_2O_2 was varied from 4.04 x 10^{-1} mM to 4.04 x 10^{-5} mM, and iron was at 0.54 or 0.11 mM with dye at 20 or 50 mM.

As with the preliminary tests, this experimental section was to determine the conditions to be used for pH testing. The condition 4.04 x 10^{-1} mM hydrogen peroxide, 1.1 x 10^{-1} mM iron, and 20 mM dye was selected and would be the best to allow improvement to be seen.

pH and Buffer Effects

This experiment investigated the effect of pH on dye degradation using reagent concentrations determined in the stirring effects experiments, iron low (1.1 x 10^{-1} mM), hydrogen peroxide (4.04 x 10^{-2} mM), and dye moderate (20 mM). Each reported data set is an average of three replicates of that test. The pH levels that were prepared in this section were adjusted to approximately 2, 5, and 7. The tests where citrate and phosphate buffers were included have a reliable pH level, but pH during tests where there were no buffers is only approximately known. The lack of buffers allowed the pH to change after the tests were prepared. Because the pH was never measured while the reaction was occurring, the pH was assumed to remain the same.

Figure 13 shows dye degradation at pH 2, 5, and 7 using solutions buffered with phosphate (25 mM) and citrate (25 mM). None of the tests were effective at removing dye. Tests with pH 7 and pH 5 showed an initial decrease and then an increase in absorbance.

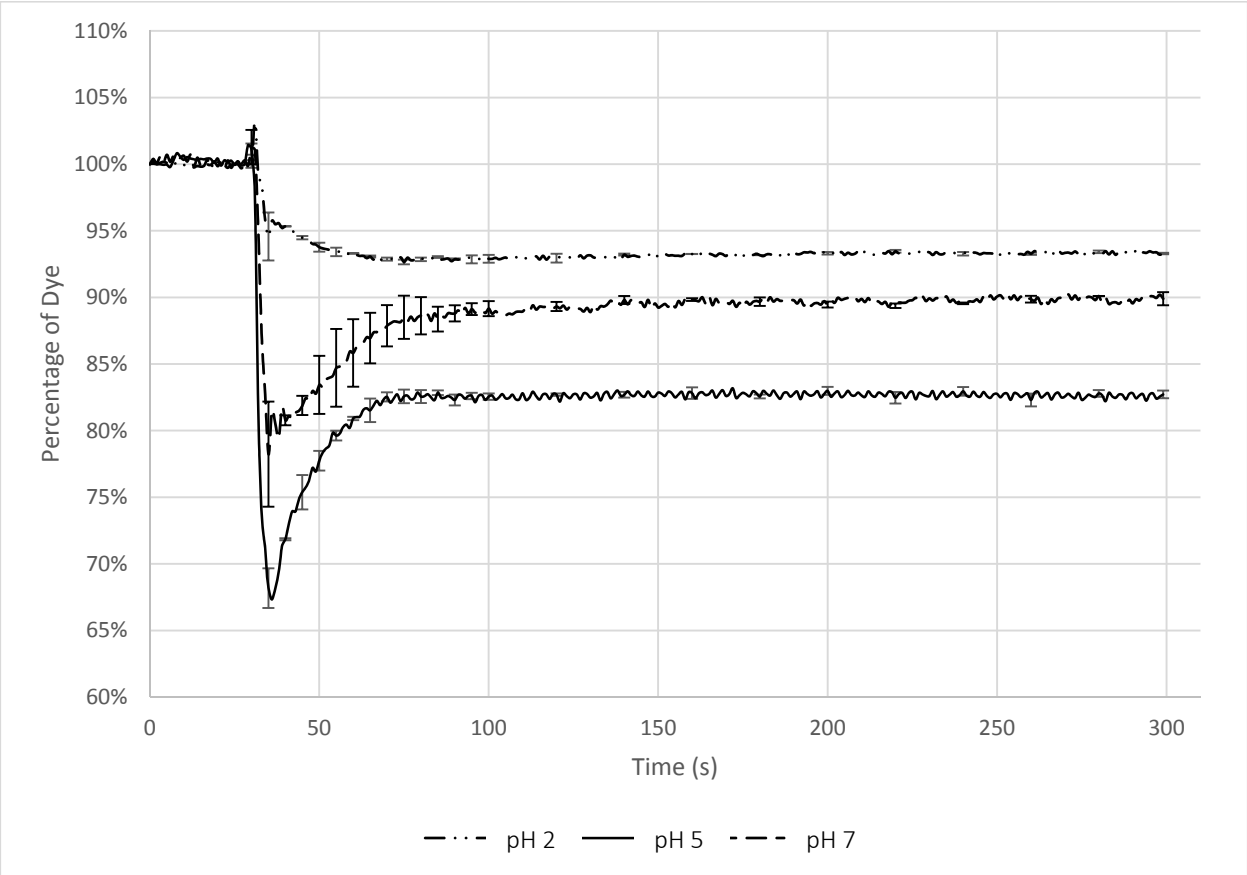

Figure 13. pH 1evels 2, 5, and 7 with the phosphate and citrate buffers and concentrations of 4.04×10^{-2} mM H_2O_2, iron 1.1×10^{-1} mM, dye 20 mM.

Figure 14 shows tests using a solution that was adjusted with only a phosphate buffer. Unlike the results illustrated in Figure 13, the tests showed degradation curves similar to ones seen in previous studies (Araujo et al., 2011; Bandala, Velasco, 2008). Tests with pH 5 were the most effective with these concentrations.

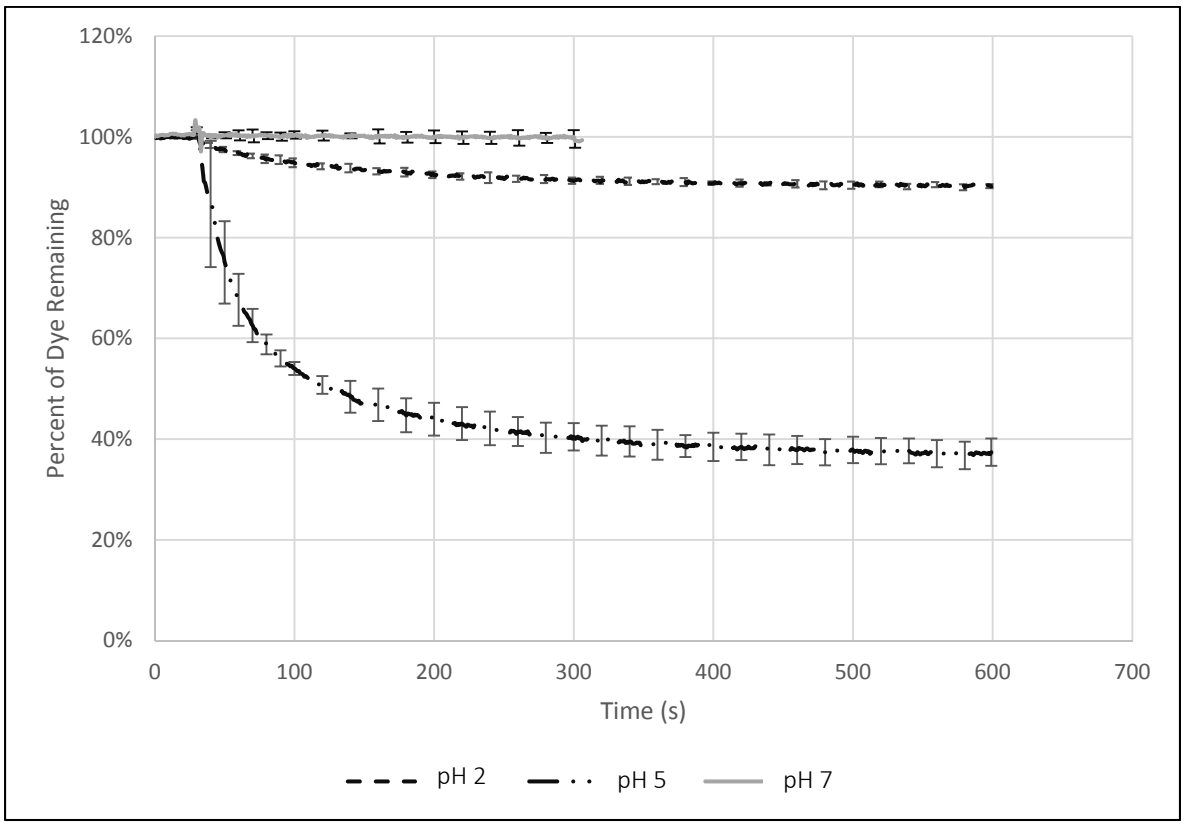

Figure 14. pH levels 2, 5, and 7 with only the phosphate buffer and concentrations of 4.04 x 10^{-2} mM H_2O_2, iron 1.1 x 10^{-1} mM, dye 20 mM.

Figure 15 shows tests with pH levels of 2, 5, and 7 adjusted without any buffer. The test using pH 7 was the most effective at removing dye with a mean of 11.9±0.2% dye remaining at the end of the test. The amount of dye remaining for the three tests from best to worst was pH 7, 5, 2 unlike the tests from Figure 14.

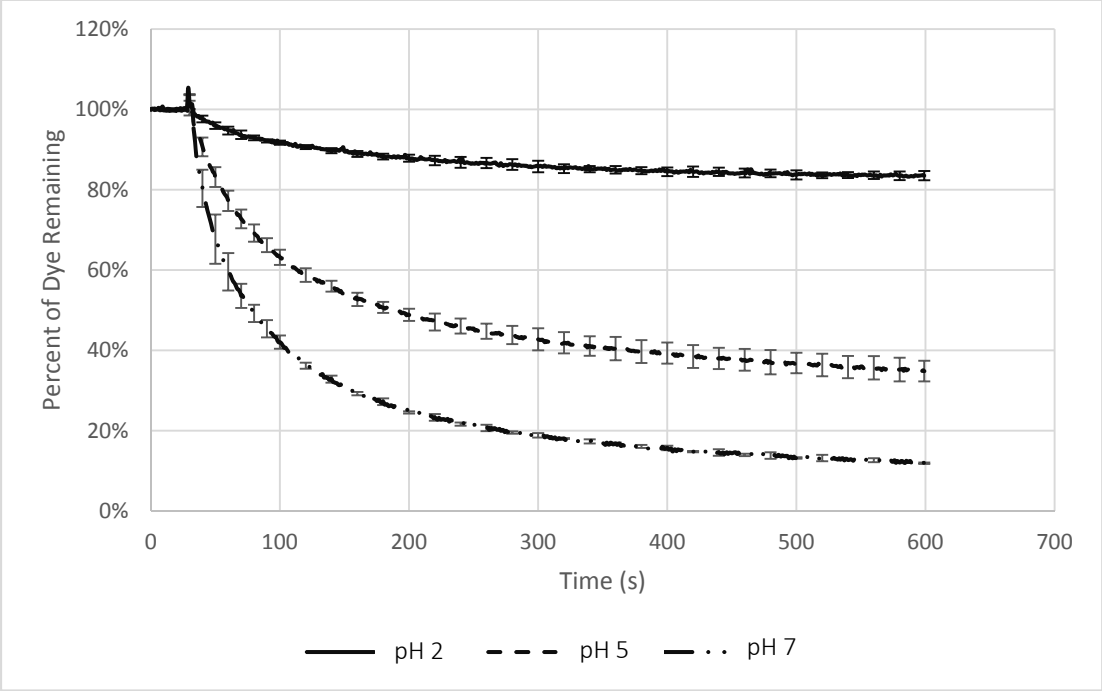

Figure 15. pH levels of 2, 5, and 7 without using buffers with concentration of 4.04 x 10^{-2} mM H_2O_2, iron 1.1 x 10^{-1} mM, dye 20mM.

Table 9 summarizes the amount of dye remaining from the various tests with pH. The tests show the worst condition with regard to pH was approximately pH 2 for all conditions. The best condition was found to be pH 7 without any buffers. The amount of dye remaining was 11.9±0.2%.

Table 9. *Average Dye Remaining for the Tests Where pH was 2, 5, and 7and pH was Adjusted without Buffers, with the Phosphate Buffer, and with Both Citrate and Phosphate Buffers*

	Percent of Dye Remaining		
Approximate pH level	**No buffer**	**Phosphate buffer**	**Citrate and phosphate buffer**
2	83.5±1.2%	90.2±0.4%	93.3±0.1%
5	34.9±2.6%	37.4±2.7%	82.7±0.3%
7	11.9±0.2%	100.1±1.1%	89.9±0.5%

CHAPTER 5: DISCUSSION AND CONCLUSION

Summary and Discussion

Preliminary Experiments

The goal of this study was to determine effective conditions to degrade the azo dye Allura red AC. During the experiment, preliminary conditions were developed to help determine effective conditions. Each reactant was tested with a low, moderate, and high concentration. Eight tests were chosen based on the reproducibility of the kinetic curve and remaining dye at the end of the reaction. If the tests had degradation curves that appeared to be largely different from one another, like the ones seen in Figure 4, or standard deviation was greater than 10%, the test was considered inconclusive.

A few patterns emerged from the eight tests. Table 5 shows hydrogen peroxide was more effective at lower tested concentrations, and Table 6 shows iron was more effective at higher tested concentrations. Tables 5 and 6 also show that dye may not affect dye degradation in these conditions. Table 7 shows that hydrogen peroxide may have more of an effect on dye removal under tested conditions, but this could be because the absolute change in hydrogen peroxide concentration was much greater from high to moderate compared to iron. Hydrogen peroxide varied from 339 mM (high) to 172 mM (moderate), iron varied from 2.2 mM (high) to 1.1 mM (low). The change in hydrogen peroxide was much greater than iron and could be the reason for hydrogen peroxide to have a bigger effect on the Fenton reaction.

The set of conditions used for stirring experiments were moderate iron concentrations (1.1mM), moderate dye concentrations (20mM), and high hydrogen peroxide concentrations (339mM) and

had an average of 26.3±3.7% dye remaining at the end of the reaction. Other conditions were able to remove more dye, but the purpose of these preliminary tests was to determine a condition that can be improved. Previous studies have shown that approximately 10% dye remaining is near the optimum the Fenton can remove (Bandala, Peláez, 2008; Chacon et al., 2005). Choosing a test with 26% of dye remaining allows room for improvement.

Stirring Effects

This set of experiments found the best set of concentrations to degrade dye involved using a cuvette stir plate. Stirring was chosen as the next experimental section because the preliminary tests section had a number of tests with inconclusive results. The amount of tests that could be chosen was 30% of the initial 27 tests, which implies the method could be improved. In addition, while performing tests in the preliminary section, it was noticed that at the end of some of the tests the dye was stratified in the cuvette. The top of the cuvette had more dye than the bottom. The stratification was likely due to the solution not being stirred, and could explain why the preliminary tests had so many inconclusive results.

Initially, the test conditions used with stirring were based on the results from the first section, but stirring caused problems in measuring the kinetic reaction. Excess hydrogen peroxide can produce oxygen. Stirring sped up the reaction, producing oxygen more quickly. Oxygen bubbles in the cuvette refracted the light used to measure the amount of color. For this reason, the original methodology of testing with the conditions moderate iron (1.1 mM), high hydrogen peroxide (339 mM), and moderate dye (20 mM) needed to change, and another set of conditions needed to be established. Establishing these conditions began by lowering hydrogen peroxide from 339 mM to 4.04×10^{-1} mM and 4.04×10^{-2} mM to fix the problem with oxygen bubbles. Although lowering the concentrations did improve the oxygen production in the test, there was still evidence that the bubbles were inhibiting the measurements of the reaction (Figure

5). Iron was then lowered to 1.1 x 10^{-1} mM and repeated to further improve measuring the reaction and to understand the reproducibility of stirring experiments. Iron 1.1 x 10^{-1} mM, H_2O_2 4.04 x 10^{-2} mM, and dye 20 mM were repeated six times and proved reliability with only 9.8±2.3% of dye remaining. These results can be seen in Figure 6 and Table 8. Table 6 in the preliminary section showed the lowest concentration of iron, 1.1 x 10^{-1} mM, was the worst set of conditions with 51.6±4.3% dye remaining. The improved dye degradation in Figure 6 and Table 8 could be due to a lowering of the hydrogen peroxide concentration. With an understanding of the reliability of stirring, different conditions of iron and hydrogen peroxide were tested to determine the limits where the Fenton reaction stops working. Tests including serial dilutions for both iron and hydrogen peroxide were performed. Based on the replicate results (Figure 6 and Table 8) and the fact that the other tests in this experiment did not have replicates it was assumed that the tests shown in Figures 7 through 12 have an approximate standard deviation of 2%.

The first set of dilution tests can be seen in Figures 7 and 8. These figures show the effect of iron concentrations from 1.1 x 10^{-1} mM to 1.1 x 10^{-5} mM with hydrogen peroxide at 4.04 x 10^{-2} mM and dye at 20 mM. Figure 8 shows that as the iron concentration was increased the effectiveness of dye degradation increased. The best concentration of iron in this test was 1.1 x 10^{-1} mM with 11% of dye remaining. Other studies with the Fenton reaction have found the best conditions result in a 5-10% dye remaining (Bandala, Peláez, 2008; Chacon et al., 2005). The iron could be getting close to being saturated in the reaction. From the tests in the preliminary section, it is likely that increasing the iron concentration would make the reaction more effective.

The next set of tests performed included five tests where hydrogen peroxide concentration was varied from 4.04 x 10^{-1} mM to 4.04 x 10^{-5} mM with iron increased to 5.4 x 10^{-1} mM and dye at 20 mM (Figure 9). The most effective condition to remove dye was hydrogen peroxide at 4.04 x 10^{-1} mM with 7% of dye remaining. The next set of tests can be seen in Figure

10. These tests include varying hydrogen peroxide concentrations from 4.04 x 10^{-1} mM to 4.04 x 10^{-5} mM with iron and dye concentrations at 1.1 x 10^{-1} mM and 20 mM respectively. For these set of tests, both concentrations of hydrogen peroxide 4.04 x 10^{-1} mM and 4.04 x 10^{-2} mM had approximately the same amount of dye remaining, which was 13%. The next set of tests performed can be seen in Figure 11. These tests include varying hydrogen peroxide from 4.04 x 10^{-1} mM to 4.04 x 10^{-5} mM with iron 1.1 x 10^{-1} mM and Dye 50 mM. The increase of dye from 20 mM to 50 mM seems to have slowed down the reaction and could be because there is more dye to be removed. If iron and hydrogen peroxide were to be stoichiometrically increased, the speed of the reaction may be increased. It is difficult to say how much dye would remain at the end of this test because it appears the reaction was not completed, but they seemed to be almost complete and it is likely the amount of dye would not be substantially lower. In the preliminary section, it was noticed that dye does not have an effect on the amount of dye removed. For the concentrations of hydrogen peroxide at 4.04 x 10^{-1} mM for all test conditions, dye concentration may not change the percentage of dye degraded. However, lower concentrations of hydrogen peroxide with dye at 50 mM was less effective compared to the other tests shown in Figures 9 and 10. This could be because a high ratio of iron to hydrogen peroxide can lead to iron competing with the dye to interact with radicals and would make iron act more as a reactant and not a catalyst in the reaction (Neyens & Baeyens, 2003).

Figure 12 shows all of the hydrogen peroxide dilution tests (Figures 9, 10, and 11) overlaid on top of each other. For all of the tests, the most effective concentrations for hydrogen peroxide were 4.04 x 10^{-1} mM and 4.04 x 10^{-2} mM. The concentrations that were decided to be used with pH testing were iron 1.1 x 10^{-1} mM, hydrogen peroxide 4.04 x 10^{-2} mM, and dye 20 mM. This condition had a dye remaining of 9.8±2.3%. The condition of iron 1.1 x 10^{-1} mM, hydrogen peroxide 4.04 x 10^{-2} mM, and dye 20 mM was the best condition tested that had some

room for improvement. The conditions with 50 mM dye were considered, but testing was limited by time and these tests were not completed after 600 seconds.

pH and Buffer Effects

For this set of experiments, citrate and phosphate buffers were tested with pH 2, 5, and 7 with the concentrations determined in the stirred experiments (iron 1.1 x 10^{-1} mM, hydrogen peroxide 4.04 x 10^{-2} mM, and dye 20 mM). The set of tests using combined citrate and phosphate buffers gave unexpected results. These results can be seen in Figure 13. The tests for pH levels at 5 and 7 gave an unusual degradation curve. Unlike a typical exponential degradation of the dye, the tests showed a sharp initial drop in absorbance followed by a gradual increase. There was no clear reason why the degradation would decrease and increase. In addition to atypical degradation curves, this test was not effective at degrading dye for all pH levels. The amount of dye remaining was never less than 83%. Citrate could scavenge radicals that would otherwise degrade dye and explain why these tests weren't effective at removing dye, but it would not explain the atypical curve (M. Hambourger, personal communication, November 13, 2015).

The second set of experiments involving only phosphate as a buffer showed an interesting result as well. The results from this can be seen in Figure 14. There was no dye removal from the tests with pH 2, and pH 5 was the most effective. The test with pH 7 was slightly better than the pH 2. It was expected that pH 7 would not effectively remove dye due to iron precipitating (Duesterberg et al., 2008; Machulek et al., 2012).

The next set of tests involved no buffers at the same pH levels as the previous tests. Like the tests with only phosphate, pH 2 was the worst at removing dye (Figure 15). Unlike the first two sets of experiments with pH, these had no buffers to affect the reaction. The amount of dye remaining without buffers was approximately 84% for pH 2. Tests with only phosphate and both phosphate and citrate had more dye remaining, with 90% and 93%. Without buffers, pH 2

removed roughly 6-9% more and could be due to the buffers affecting the reaction by binding with iron, which would prevent it from participating in the reaction or by savaging radicals preventing dye from degrading. The tests of pH 5 with and without phosphate were very similar. Both had approximately 35% of dye remaining.

The test with pH 7 did the opposite of what was expected. The amount of dye remaining with this test was 12%. As stated before, this pH level is supposed to inhibit the Fenton reaction. There are several possible explanations for this result. The lack of buffers may have allowed the pH to be lower than pH 7. The tests were completed by adding 2.34 mL of pH 7 DI water with 0.06 mL of the iron stock, which had a pH of approximately 2. In addition, carbon dioxide was produced through the reaction, which can acidify the solution. The pH levels were not measured during the kinetic reaction, so the pH during the solution is unknown. The litmus test at the end of the test with pH 7 and no buffer showed the pH was approximately 4 or 5. The pH during the reaction could have been low enough to allow iron to stay in solution and participate in the reaction. It is also worth noting that the experiments in the stirring effects section (Figure 6 and 8) used the same concentrations of iron, hydrogen peroxide, and dye concentrations as the test with pH 7 without buffers (Figure 15). This set of conditions for removing dye from that section had 10-15% remaining at the end of the tests. The pH of the tests for the stirring effects section was never measured or controlled. The stock DI water for the tests in the stirring effects section was approximately pH 6-7. The pH levels at the time of the test during the stirring effects could have been similar to the test where pH was adjusted to 7 without buffers. Another possible reason for pH 7 being effective at removing dye is the dye Allura red influencing the reaction. Some studies have found that certain dyes can facilitate the Fenton reaction to perform better at high pH levels (E. Bandala, personal communication, November 20, 2015). Another azo dye may produce different results.

Future Studies

Future studies could include testing actual hair salon wastewater and the use of AOPs. The dye used in this study would likely not be found in salon wastewater, and this study controlled the organic material that was degraded. Salon wastewater would have other organic materials, such as other types of dye and surfactant, with various concentrations. There has been much discussion on AOPs and their potential for degrading dyes. This study is the first step for incorporating the use of AOPs for a salon greywater system. More studies need to be done to understand how these findings might change under different methodologies such as incorporating a photo-reactor. In additions, the tests where pH was adjusted to 2, 5, and 7 showed unexpected results. Tests where buffers were used to control pH had unexplainable results (Figure 13 and 14). Tests with pH 7 and no buffers were effective at removing dye by having 12% of dye remaining (Figure 15). The reason for pH 7 being so effective could be that pH was not truly 7 or the dye Allura red may facilitate the reaction, but more testing is needed.

Possible Discrepancies

Throughout the first and second experimental section, there were day-to-day variabilities on occasion. The variabilities could have been due to pH not being controlled with buffers. The pH could have changed from day to day, changing results slightly. The preliminary tests (Tables 5, 6, and 7) had only 30% of the 27 tests giving acceptable data, which was likely due to a lack of stirring because the cuvette showed stratification of dye at the end of the tests. The reported data may have different results if repeated with stirring.

Conclusions

The Fenton reaction can be used to effectively remove dye from water. Some variables that influence the Fenton reaction include the concentrations of iron, dye, hydrogen peroxide, and pH levels. A set of conditions that are effective includes concentrations of iron 1.1×10^{-1}

mM or 5.4 x 10^{-1} mM, dye 20mM, and hydrogen peroxide 4.04 x 10^{-1} mM or 4.04 x 10^{-2} mM. The best pH to use with that set of conditions is unclear. An approximate pH of 2.5 to 5 is likely the best case. The pH was not controlled for most of the tests in this study but was likely around 3 to 5. In the experiments where pH was controlled, pH 2 was never successful at removing dye. Tests with pH 7 were unsuccessful for all tests except the test without buffers. In addition, the Fenton reaction has been studied extensively with other types of dyes in other types of methods, and the range of pH 2.5 to 5 is typically found to be successful (Bandala & Raichle, 2013; Bandala, Velasco, 2008; Cheng et al., 2004; Duesterberg et al., 2008; Dunford, 2002).

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Vita

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